

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representation of
The original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

THIS PAGE BLANK (USPTO)

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 85107704.0

(51) Int. Cl.⁴: **B 01 J 2/28**

(22) Date of filing: 21.06.85

(30) Priority: 25.06.84 US 624301

(43) Date of publication of application:
29.01.86 Bulletin 86/5

(84) Designated Contracting States:
CH DE FR GB IT LI NL

(71) Applicant: **The B.F. GOODRICH Company**
Dept. 0015 WHB-6 500 South Main Street
Akron, Ohio 44318(US)

(72) Inventor: **Mollinger, Paul James**
32354 Redwood Boulevard
Avon Lake Ohio 44012(US)

(72) Inventor: **Kuo, Charles Chia-Chuen**
33362 Karen Drive
Avon Lake Ohio 44012(US)

(74) Representative: **von Kreisler, Alek, Dipl.-Chem. et al,**
Deichmannhaus am Hauptbahnhof
D-5000 Köln 1(DE)

(54) **Process for pelletization of powder materials and products therefrom.**

(57) **A method for the production of small, dustless, free-flowing pellets of powder chemical additives utilizing a high molecular weight polymeric binder, such as polyvinyl alcohol; a surfactant containing oxyethylene groups; and water.**

PROCESS FOR PELLETIZATION OF POWDER
MATERIALS AND PRODUCTS THEREFROM

BACKGROUND OF THE INVENTION

The market demand for dustless and free-flowing chemical products has increased significantly and is likely to continue in this trend. The demand for dust-free, flowable materials is especially high in the compounding of rubber and polymeric compositions.

The use of finely divided materials in compounding of natural and synthetic rubber presents dusting problems which may have adverse consequences relative to productivity, contamination, environmental pollution, and safety. The finely divided nature of most rubber additives causes them to be blown into the air during production operations such as conveying, mixing or milling. This results in a production efficiency reduction due to the loss of some additives. Additionally, the dusting problem can result in the possible contamination of other materials. Further, airborne dust causes environmental and housekeeping problems, as well as safety hazards created by the explosive nature of finely divided dust. Bridging problems of powder materials also adversely affect their use in automatic feeding systems. Thus, it is desirable to have rubber and polymer additives in a dustless, free-flowing form with good dispersion properties so that processors can meet environmental regulations, application needs, and implement automatic feeding systems for improved productivity.

Efforts have been made in the art to eliminate the problems associated with finely divided materials by converting such materials into agglomerates. To form such agglomerates, generally an

agglomerating agent must be added to the finely divided materials. Frequently, this agglomerating agent has been a material which was objectionable when mixed into a rubber compound with which the finely divided material was used. Some of the prior art agglomerates were cohesive and thus not free-flowing, and do not lend themselves to normal or automatic handling and weighing procedures. Some materials employed for preparing prior art agglomerates were used in such large amounts that they diluted the rubber ingredients or did not readily disperse in rubber during mixing.

In many of the prior art agglomerates, the pellet crush strength was either too low or too high. Agglomerates with too low of a crush strength are undesirable because of their inability to withstand normal shipping and handling. Agglomerates having too high of a crush strength generally had poor dispersing properties and did not mix well. Typical processes for agglomerating powder materials are disclosed in U.S. patent nos. 4,362,559; 4,194,901; and 4,298,858; Canadian patent no. 890,833; Japanese patent nos. 78 90,116; 78 66,923; 8,205,731 and 82,192,439; and Czech patent no. 185,383.

It is the objective of the present invention to solve the above problems associated with powder materials and prior art agglomerates by providing a pelletization process for making small, dustless, and free-flowing products which have good dispersion properties. It is a further objective of the present invention to produce pellets of chemical additives which have a very low level of agglomerating agents and other processing aids. A major advantage of the present invention is the production of pellets with a pellet crush strength range suitable for both shipping

and effective dispersion, which is controllable to custom specifications.

SUMMARY OF THE INVENTION

This invention relates to a method for producing dustless pellets from powders, particularly powder additives for rubber and polymers, which comprises using a processing aid system essentially containing an effective amount of 1) a high molecular weight water-soluble polymeric binder, 2) an organic surfactant, and 3) water. The polymeric binder is preferably polyvinyl alcohol or a cellulose derivative. The surfactant preferably contains a polyoxyethylene group. The current method is particularly suitable for the formation of pellets by a screw extrusion process and yields small, dustless, and free-flowing pellets which have good dispersion properties which equal or exceed that of the powder.

DETAILED DESCRIPTION

The present invention relates to a novel method for the production of dustless pellets from powders and to the pellet products produced thereby. The method comprises using a processing aid system essentially containing an effective amount of a high molecular weight water-soluble polymeric binder, an organic surfactant, and water. Although the method may be carried out utilizing a variety of agglomeration techniques, such as roll pressing, pellet milling, spray drying, and screw extrusion, the method is particularly suitable for pellet formation using screw extrusion.

Powders which are suitable for pelletization utilizing the present invention can be any water insoluble chemical powder used as a process additive. The present method is particularly suited for pelleting powders of organic rubber chemicals and chemical additives for plastic polymers. Suitable

powders include, for example, accelerators, vulcanizing agents, pigments, stabilizers, antioxidants, fillers, curing additives, reinforcing agents, and the like.

Binders are essential aids to economic and effective agglomeration of solids. In the screw extrusion process particularly, the pressure applied is not sufficiently high for compaction and a binder is needed to agglomerate the powders. In order to obtain uniform pellet strength with a very low processing aid ingredient content in the final product, high molecular weight water soluble polymeric binders are used in practicing this invention. These high molecular weight polymeric binders work well with water to provide a thin film between powder particles, and to entangle the particles into agglomerates which exhibit improved plasticity under shear force and pressure. Suitable polymeric binders for the practice of this invention include most water-soluble film-forming resins; for example, partially and fully-hydrolyzed polyvinyl alcohols, polyacrylamides, acrylamide-acrylic acid copolymers, starches, polyacrylic acids, ethylene oxide polymers and alkyl and hydroxyalkyl cellulose derivatives, such as, for example, methyl cellulose, hydroxy propyl methyl cellulose, hydroxy ethyl cellulose and the like. Suitable concentration of binder ranges from about 0.2 to about 4 parts by weight per 100 parts of dry powder, preferably from about 0.2 to about 2 parts. The preferred binder is a polyvinyl alcohol or an alkyl or hydroxyalkyl cellulose derivative. Most preferably the polyvinyl alcohol has a molecular weight of 10,000 or greater.

The present invention involves the use of an organic surfactant to obtain pellets having the desired characteristics. Suitable organic surfactants

include, for example, water soluble or dispersible nonionic surfactants, propylene glycols and polymeric surfactants such as the polyoxyethylene derivatives. The preferred organic surfactants for the practice of this invention are the polyoxyethylene derivatives, such as, for example, polyoxyethylene acids, polyoxyethylene alcohols, oxyethylene-oxypropylene copolymer, and the like. More preferably the organic surfactant contains more than two oxyethylene units, and most preferably the surfactant is a polyoxyethylene oleyl ether or a polyoxyethylene stearate. In order to work effectively in the present invention, the surfactant must be stable with the powder chemical additives, especially with accelerators, during processing and storage, and must be fairly soluble in water. Specifically, polyoxyethylene (10) oleyl ether, polyoxyethylene (20) oleyl ether, and polyoxyethylene (50) stearate were found to work well in the process of this invention.

The use of an organic surfactant is critical for the practice of the present invention regardless of the method of agglomeration used. The use of a surfactant is especially important in pelletization by the screw extrusion process. The surfactant makes the production of desired pellets with screw extrusion possible and provides the following multi-functions:

1) The surfactant serves as a wetting agent to help the aqueous solution wet the particle surfaces of organic powder. Wetting is important for uniformly spreading the binder on powder particles to provide good and uniform binding and reduces the amount of binder required.

2) The surfactant serves as a lubricant and plasticity improving agent. This improves the plasticity of the whole mass and makes it easier to

extrude into the desired shape. This also reduces extruder power requirements and increases extruder output.

3) Most importantly, the surfactant acts as a pellet crush strength controller. By adjusting the ratio of primary binder and surfactant, plasticity, ingredient content, and pellet strength can be controlled to desired levels. Suitable levels of surfactant ranges from about 0.2 to about 1.0 parts by weight per 100 parts of dry powder.

Another important component of the processing aid system used in the practice of this invention is water. The primary function of water is to dissolve and carry ingredients such as the binder and surfactant. Water works with the binder and surfactant to provide the lubrication between particles and plasticity for the whole mass. Water also contributes binding action through capillary force in the wet pellet due to its high surface tension. The amount of water needed to wet the particle surface and fill the space between the particles is determined by the particle size, shape, and other properties of the powder particles. Typically the amount of water ranges from about 10 parts to about 45 parts by weight per 100 parts of dry powder. The water may be added directly to the binder and surfactant or it may be present in wet filter cakes of the powder chemical additives. Where wet filter cakes of the additives are used, the dry binder and surfactant may be added to the filter cakes by blending prior to the pelletization step.

In the preferred embodiment of this invention, three main steps are involved, i.e., mixing, extruding and drying. Other agglomerating techniques may be used instead of extrusion, such as, for example, roll pressing, pellet milling, and spray

drying. The binder and the surfactants can be dissolved or dispersed in water and subsequently mixed with the dry powder. The dry binder and surfactant can also be mixed with wet powder and then fed to the extruder. The mix is agglomerated through a screw extruder into extrudates. The extrudates are then broken into short pellets either outside or inside of a dryer and dried in the dryer. The present process allows the pellet cutting or breaking to be performed with the minimal generation of fines. In the process, about 98% of the powder is converted to pellets and less than 2% as fines.

Good mixing is important for uniformly spreading liquid and processing aids on the powder particle surfaces, and any conventional mixing equipment may be used. Good mixing provides the uniformity of feed material for extruding and, thus, the uniform quality of the final product.

The present invention yields small, dustless, free-flowing pellets with a satisfactory crush strength and a low level of processing aid ingredients. These pellets can meet the needs of practically all applications in the rubber and plastic industries. Pellet crush strength is important for shipping and for dispersion. If the pellet is too soft, it cannot withstand shipping and handling conditions, but if it is too hard it causes dispersion problems during compounding. Pellet crush strength is measured by applying weight on the pellet until it is crushed and then dividing the total weight applied by the cross-sectional area of the pellet incurring the weight. A pellet crush strength in the range of about 10 to about 40 gm/mm² is preferred for effective shipping and dispersion. One major advantage of the present process is that the pellet strength can be adjusted by changing the amount of binder and

surfactant utilized. Pellets having crush strengths from about 5-100 gm/mm² are obtainable.

The flexibility of making a wide range of uniform pellet sizes is another major advantage of this process. Preferably the pellet size ranges from about 0.5mm to about 2mm in diameter and from about 2mm to about 4mm in length. Small pellets of this size exhibit better dispersion and flowability properties. The pellets are preferably cylindrical in shape and have an angle of repose smaller than 40°.

After the pellets are dried, the processing aid ingredients in the final pellet product essentially consist of binder and surfactant. A suitable final pellet product should contain about 4% or less of processing aid ingredients on a dry weight basis; preferably about 2% or less; and most preferably less than 1%.

To illustrate this invention, pellets were made following the present inventive process from dry powders of accelerators for rubber. In each example, the binder and surfactant were dissolved in water and subsequently mixed with the dry accelerator powder. The mix was then screw extruded, pelletized, dried and evaluated. The specific recipes used are given in Table I. In all Examples 100 parts by weight of dry accelerator powder were used.

TABLE I

	<u>EXAMPLES</u>			
	I	II	III	IV
<u>Accelerator (100 pbw)</u>	<u>(OTOS)</u>	<u>(BBTS)</u>	<u>(OMTS)</u>	<u>(MBTS)</u>
Binder (Polyvinyl Alcohol)	0.25	0.75	0.40	0.25
Surfactant (Polyoxyethylene oleyl ether)	0.25	0.50	0.60	0.20
Water	14	40	22	43

OTOS= N-oxydiethylene thiocarbamyl N'-oxydiethylene sulfenamide

BBTS= N-t-butyl-2-benzothiazole sulfenamide

MBTS= 2-mercapto benzothiazole disulfide

OMTS= MBTS/N-oxydiethylene-2-benzothiazole sulfenamide

All amounts are parts by weight.

In all Examples, essentially dustless, cylindrical pellets were made. The pellets were free-flowing and had angles of repose smaller than 45°. The pellet crush strength in the Examples ranged from 20-35 grams/mm². Pellet sizes ranged from 1 to 2mm in diameter and from 1 to 4mm in length. Pellet size was uniform with nearly all the particles being retained on 10-12 mesh screens.

Pellets of OTOS made by the present process were evaluated in a typical styrene-butadiene rubber stock. Vulcanizates of the stock were cured for 15 minutes at 320°F (160°C) and tested for stress/strain properties. The OTOS pellets were compared to an equivalent amount of powder to evaluate dispersibility. Poor dispersibility is usually reflected by a lower

tensile strength and lower elongation. The results are presented in Table II.

	<u>TABLE II</u>	
	OTOS Powder	
	<u>(control)</u>	<u>OTOS Pellet</u>
Tensile strength (psi)	2744	3016
Elongation (%)	526	566
300% modulus (psi)	1319	1322

CLAIMS

1. A method for producing dustless pellets from powders which comprises combining the powders with a processing aid system containing essentially of an effective amount of a high molecular weight water-soluble polymeric binder, an organic surfactant, and water.
2. A method of Claim 1 wherein the polymeric binder is selected from the group consisting of partially-hydrolyzed polyvinyl alcohols, fully-hydrolyzed polyvinyl alcohols, alkyl cellulose derivatives and hydroxyalkyl cellulose derivatives.
3. A method of Claim 1 wherein the surfactant is a polyoxyethylene alcohol or acid derivative.
4. A method of Claims 1 to 3 wherein the powder chemical additives are selected from the group consisting of N-oxydiethylene thiocarbamyl N'-oxydiethylene sulfenamide, N-t-butyl-2-benzothiazole sulfenamide, 2-mercapto benzothiazole disulfide, and N-oxydiethylene-2-benzothiazole sulfenamide; and the surfactant is a polyoxyethylene oleyl ether or a polyoxyethylene stearate.
5. A method of Claim 1 wherein said pellets are formed by screw extrusion.
6. A method of Claim 5 wherein the pellet size ranges from about 0.5 to about 2mm in diameter and from about 2 to about 4mm in length; and the pellets have a pellet crush strength which ranges from about 10 to about 40 grams/mm.
7. A pellet product comprising one or more organic rubber chemicals, a high molecular weight water-soluble polymeric binder, and an organic surfactant.

8. A pellet product of Claim 7 wherein the polymeric binder is selected from the group consisting of partially-hydrolyzed polyvinyl alcohols, fully-hydrolyzed polyvinyl alcohols, alkyl cellulose derivatives, and hydroxyalkyl cellulose derivatives.

9. A pellet product of Claim 7 wherein the surfactant is a polyoxyethylene alcohol or acid derivative.

10. A pellet product of Claims 7 to 9 wherein the organic rubber chemicals are selected from the group consisting of N-oxydiethylene thiocarbamyl-N'-oxydiethylene sulfenamide, N-t-butyl-2-benzothiazole sulfenamide, 2-mercaptobenzothiazole disulfide, and N-oxydiethylene-2-benzothiazole sulfenamide; and the surfactant is a polyoxyethylene oleyl ether or a polyoxyethylene stearate.



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 169 382
A3

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 85107704.0

(51) Int. Cl.⁴: **B 01 J 2/28**

(22) Date of filing: 21.06.85

(30) Priority: 25.06.84 US 624301

(43) Date of publication of application: 29.01.86
Bulletin 86/5

(84) Designated Contracting States: CH DE FR GB IT LI NL

(88) Date of deferred publication of search
report: 27.07.88 Bulletin 88/30

(71) Applicant: The B.F. GOODRICH Company,
Dept. 0015 WHB-6 500 South Main Street, Akron,
Ohio 44318 (US)

(72) Inventor: Mollinger, Paul James, 32354 Redwood
Boulevard, Avon Lake Ohio 44012 (US)
Inventor: Kuo, Charles Chia-Chuen, 33362 Karen Drive,
Avon Lake Ohio 44012 (US)

(74) Representative: von Kreisler, Alek, Dipl.-Chem. et al,
Deichmannhaus am Hauptbahnhof, D-5000 Köln 1 (DE)

(54) Process for pelletization of powder materials and products therefrom.

(57) A method for the production of small, dustless, free-flowing pellets of powder chemical additives utilizing a high molecular weight polymeric binder, such as polyvinyl alcohol; a surfactant containing oxyethylene groups; and water.

EP 0 169 382 A3



European Patent
Office

EUROPEAN SEARCH REPORT

0169382

Application Number

EP 85 10 7704

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	GB-A- 975 847 (MONSANTO) * Page 1, lines 58-65; page 2, lines 24-38; page 2, lines 70-79; page 2, lines 119-123 *	1,4,5,6 ,7,10	B 01 J 2/28
X	GB-A- 891 537 (I.C.I.) * Page 3, lines 103-110; page 4, lines 5-9 *	1,4-7, 10	
X	DE-A-2 040 229 (KA0 SOAP) * Page 2, paragraph 5; page 3, paragraphs 1,2,4; page 4, paragraph 1 *	1,2,3,7 ,8,9	
A	FR-A-2 488 813 (TOYO SODA MANUFACTURING) * Page 2, lines 15-32; page 3, lines 27-35; page 4, lines 2-7; page 5, lines 1-34 *	1,3,4,9 ,10	
A	US-A-3 018 261 (A. VON FRIEDRICH et al.) * Column 2, lines 22-52; column 3, lines 13-14 *	1,2,5,8	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	EP-A-0 021 263 (BAYER) * Page 3, lines 16-26; page 6, lines 6-19; page 10, lines 5-8 *	1,2,3,7 ,8,9	B 01 J C 08 K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14-04-1988	Examiner KERRES P.M.G.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	